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Boulder damage symposium annual thin film laser damage competition

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ABSTRACT

Optical instruments and laser systems are often fluence-limited by the multilayer thin films deposited on the optical surfaces. When comparing publications within the laser damage literature, there can be confusing and conflicting laser damage results due to differences in testing protocols between research groups studying very different applications. In this series of competitions, samples from multiple vendors are compared under identical testing parameters and a single testing service. Unlike a typical study where a hypothesis is tested within a well-controlled experiment with isolated variables, this competition isolates the laser damage testing variables so that trends can be observed between different deposition processes, coating materials, cleaning techniques, and multiple coating suppliers. This series of damage competitions has also been designed to observe general trends of damage morphologies and mechanisms over a wide range of coating types (high reflector and antireflector), wavelengths (193-1064 nm), and pulselengths (180 fs – 13 ns). For each of the competitions, a double blind test assured sample and submitter anonymity so only a summary of the deposition process, coating materials, layer count and spectral results are presented. In summary, laser resistance was strongly affected by substrate cleaning, coating deposition method, and coating material selection whereas layer count and spectral properties had minimal impact.

Keywords: laser damage testing, mirror, antireflector, thin film, multilayer, excimer laser, femtosecond laser, nanosecond laser, near infrared laser, ISO21254-2

1. INTRODUCTION

In 2008, a thin film laser damage competition was launched at the Boulder Damage Symposium with a 1064 nm normal incident high reflector tested with a 5 ns pulse length.¹ In subsequent years at the Boulder Damage Symposium, thin film damage competitions were held for a 786 nm femtosecond (180 fs) normal incident high reflector², a 351 nm antireflection coating tested with 7.5 ns pulses³ and finally a normal incident 193 nm excimer mirror damage tested with 13 ns pulses.⁴ In each competition, it was observed that a wide range of laser resistance exists between the worst and best samples ranging from a factor of 5× for the femtosecond mirrors to over 100× for the 1064 nm nanosecond mirrors. Other trends were observed such as the impact of surface preparation, coating material selection, and deposition method with often very different results observed depending on the wavelength, pulse length, and coating type of the various competitions.

2. PARTICIPATION

Over the history of this damage competition, a total of thirty-seven companies have participated representing six different countries (China, Germany, Japan, Lithuania, United Kingdom, and the United States). A full list of the participants and the years of participation are listed in table 1. The damage testing was donated by either Spica (1064 nm HR and 351 nm AR) or Laser Zentrum Hannover (786 nm femtosecond HR and 193 nm excimer HR). The number of annual submissions per participant was requested not to exceed two so as to minimize the number of required damage tests. Participants that submitted multiple samples tended to isolate variables such as cleaning techniques or coating materials to gain a better understanding of the most significant process parameters for high laser resistance.

3. SAMPLES

The substrates for this series of competitions were all provided by the participants. For the 1064 nm HR and 786 nm femtosecond HR mirror coatings, 50 mm BK7 substrates were specified. For the 351 nm AR coating, 50 mm fused silica samples were required. Because the substrate finish can have a significant impact on the laser resistance of an AR coating, both coated and uncoated samples were submitted by each participant. For the 193 nm excimer HR coating, the substrate dimension was reduced to 38.5 mm because of the high cost of calcium fluoride which was used as substrates by two of the participants. The remaining participants submitted excimer HR coatings on fused silica substrates. All substrates had a thickness requirement of 10 mm. The objective was to have identical and unmarked substrates to maintain the anonymity of the samples. Substrates were transferred to identical plastic cases each marked with a vendor code. The identity of the suppliers and participant code was only known by an administrative assistant to maintain a double blind experiment. The author and damage testing service only had access to the participant code so as to remain unbiased and to protect the identities of participants whose samples had lower laser resistance. At the completion of the damage testing each participant was informed of their unique vendor code and damage threshold result.

Specifications for the four competitions are listed in table 2. In addition, the environmental requirements were ambient lab conditions (40% relative humidity and 20 degrees Celsius). There were no stress or reflected wavefront requirements. Participants each provided spectral data to validate spectral performance. Participants also provided a brief description of the coating deposition process, coating materials, and the layer count.

A total of fifteen different coating materials have been used over the four damage competitions including fourteen different oxides and one metal (gold). The refractive index and UV cutoff for the oxide materials are illustrated in figure 1. The deposition processes that have been used include electron-beam, ion assisted deposition, plasma assisted deposition, ion beam sputtering, magnetron sputtering, advanced plasma source, sol gel, and resistive evaporation. Minor variations of these processes like the inclusion of enhanced oxygen were also reported.

4. DAMAGE TESTING

Damage testing was performed by two different testing services. Spica tested the 1064 nm high reflector and the 351 nm antireflection coating using the NIF testing method described by Borden.⁵ Lazer Zentrum Hannover (LZH) tested the 786 nm femtosecond high reflector and the 193 nm excimer mirror using the ISO 21254-2 test.⁶

The ISO test is very well suited to testing optical coatings whose damage thresholds are limited by intrinsic properties or have a uniform damage threshold across the optic. The ISO test is done in the 10,000:1 mode over 150 sites so the test is also very well suited to statistically determine the damage threshold for a single shot and an infinite number of pulses. The damage thresholds for short wavelength (excimer laser) and short pulse (femtosecond laser) tend to be limited by intrinsic properties of the coatings, hence the ISO test method was deemed most suitable.

The NIF damage test involves scanning over a 1 cm^2 area with 2,400 sites starting at 1 J/cm^2 and increasing in 3 J/cm^2 increments so laser conditioning⁸⁻⁹ can occur in the testing area. Damage was classified into three categories, “No Damage”, “Initiation”, and “Failed”. “No Damage” is defined as no visible change to the coating. “Initiation” is pinpoints as large as $100 \text{ }\mu\text{m}$ are

observed, however, none of the pinpoint damage grew upon repeated illumination. “Fail” is defined as the fluence where pinpoint damage exceeded 100 μm , pinpoint damage grew upon repeated illumination, or pinpoint damage occurred in more than 1% of the total number of sites. The 351 nm antireflection coating and the 1064 nm high reflector both tend to be limited by coating defects so they have a non-uniform laser resistance across the coating. Therefore, they were tested by the larger area NIF protocol. More detailed descriptions of the setup and testing protocol can be found in the ISO standard and NIF damage test paper.⁵⁻⁷

Damage was detected by either a visual inspection or an on-line scatter detector. In both cases, the pulse train was stopped when damage growth was observed. After the irradiation procedure, each sample was inspected by interference contrast microscopy (Nomarski-microscope) with magnification adapted to the observed morphology and size of damage sites.

5. RESULTS

The results of the four damage competition are discussed below. Typically coating material and deposition had the largest impact on the laser damage resistance of the samples, however, the relative impacts of these variables depended greatly on the coating type, wavelength, and pulselength. The number of layers and spectral characteristics has little impact on the laser resistance.

5.1 1064 nm high reflector

The damage threshold results are shown in figure 2 and illustrate a $>100\times$ difference between the highest and lowest laser damage threshold values. From a no damage perspective, the coating with the higher laser resistance was deposited by e-beam. For this particular sample a plasma

etch was used to clean the sample before deposition. The details of this process were not provided, although given how well this sample performed, it will likely create significant interest within the thin film community and hopefully lead to future publications. It is possible that defects are ejecting from this sample, but may be undetected because the pinpoints do not scatter more light than before ejection. Although unproven, it is likely that the plasma etch increases the adhesion of the multilayer to the substrate which could lead to smaller ejection sites. Comparison of the irradiated and non-irradiated section of the sample could provide insight into why the sample did so well, however to protect company proprietary information no microscopy analysis occurred.

The top two coatings were deposited by e-beam, however, high laser resistant coatings were also deposited by IAD and IBS indicating that a number of deposition techniques offer promise for producing high quality laser resistant coatings for the tested parameters. The grating technology which reported extremely high thresholds for an antireflection surface at the 2007 BDS conference¹⁰ performed poorly in this competition. Very little development occurred before these samples were manufactured. Process optimization such as selection of different coating materials as illustrated in figure 7 or imprinting in a thick overcoat previously discussed for compression gratings¹¹⁻¹³ might help produce higher laser resistance. A significant advantage of this technique is the low layer count which can't support large inclusions and only very small nodular defects. Hopefully as this technology matures, advances are reported.

Hafnia is clearly the most laser resistant high index material for the coatings that were submitted. Unfortunately a large number of participants declined to share information about their coating materials thus denying readers an opportunity to learn both materials that perform well or poorly.

As expected, oxide materials clearly performed better than metallic films for the test pulse length and wavelength of this competition. The second most popular high index material in this study is tantala which clearly had an average lower laser resistance. Although tantala films generally have less scatter and fewer defects than hafnia coatings, it is more challenging to produce fully stoichiometric films. It is the author's experience that high laser resistant tantala coatings can be manufactured, although the process is significantly more difficult to develop than for hafnia films.

The final parameter that was explored in this study was evaluation of the impact of overcoats on laser resistance. Typically the first layer in a high reflector coating would be the high index to take advantage of the reflectivity achieved by large contrast in refractive indices. For the same reason high reflectors based on quarter-wave designs end with the high index material leading to an odd number of layers. It has been shown that the laser resistance of high reflector coatings can be increased with an overcoat of a low index material.¹³⁻¹⁴ Typically overcoats are half-wave in optical thickness so are optically absentee meaning they don't reduce the reflectivity and would result in an even number of layers in the multilayer stack. With these assumptions, the data was analyzed by layer count to see if a pattern would emerge with respect to an odd versus even number of layers. No cross sections were made of the coatings to quantitatively determine the actual presence of overcoats and their respective physical thicknesses to protect the proprietary designs of each participant.

Coatings with hafnia tend to perform better on average with an even number of layers indicating that overcoats may be helpful. Multilayer coatings with tantala tend to perform the same for both even and odd layer counts indicating for this material overcoats make little difference. For

both high index material multilayer coatings, it does not appear that there are any strong trends of laser resistance with respect to fewer or a greater number of layers.

5.2 786 nm femtosecond high reflector

The short pulse mirrors had only a 5:1 difference between the highest and lowest laser resistance compared to the long pulse (5 ns) 1064 nm high reflector coatings that had over a 100:1 difference. Clearly femtosecond laser damage is much more intrinsic in nature.^{16,17} There was only a 20% difference between the laser resistance of the best hafnia, titania, and zirconia coatings. All of these materials are dioxides compared to the pentoxides, niobia and tantalum, that did not perform nearly as well. Hafnia was clearly the most laser resistant high index material for long pulse coatings.

Plasma pre-etching of the surface had a favorable impact on the laser resistance of one of the samples, but not nearly to the magnitude observed in the long pulse mirror coating. Because of the expected intrinsic damage behavior, reduced electric-field designs were also submitted yielding the highest laser resistant coating of the group. Electric-field reduction techniques consist of modifying the thicknesses of the outer layers (thinner high index and thicker low index layers) to reduce the electric field in the high index layers which tend to limit the laser resistance of the coating.¹⁸ Typically the electric field is elevated in the silica layers, however, this material tends to be more laser resistant leading to a multilayer coating with an overall improved laser resistance.

The coatings with the fewest number of layers had a lower laser damage resistance. This is more likely related to the choice of pentoxide high index materials with greater refractive indices than

the oxide materials resulting in a greater contrast between materials to enable fewer layers to achieve the reflectivity specification. Coatings with an odd number of layers typically have a half-wave thickness overcoat although cross sections were not performed of the samples to protect the proprietary designs of each participant. There was no strong correlation between the laser resistance of an even and odd number of layers suggesting that overcoats are not particularly helpful or detrimental for short pulse high reflectors. No significant correlation in laser resistance was found as a function of reflectance with the exception lower reflectivity mirrors with pentoxide coating materials tended to have lower thresholds.

5.3 351 nm antireflection coating

A 60:1 difference in laser damage threshold was observed for the coated and uncoated samples as can be observed in figure 4. This wide range implies that there are significant differences within the coating industry in the understanding of the critical process parameters necessary to manufacture high laser resistant UV antireflection coatings. An additional striking observation from figure 4 is the consistent high laser resistance of sol gel coatings. Although these coatings are mechanically weak and prone to spectral degradation in the presence of outgassing contaminants, they remain the deposition process of choice for most large high energy laser systems across the world. Sol gel coatings have the advantage of being single layer coatings due to the extremely low refractive index achieved by a porous silica layer, eliminating the need for the low laser resistant high or medium refractive index materials.

Another result of the data plotted in figure 4 is the lack of significant difference between the best magnetron sputtered and electron beam deposition coatings suggesting that it is the process details that are more important than the process type for this class of coating. Only two different

participants contributed coatings deposited by ion beam sputtering and one participant submitted coatings deposited by resistive evaporation. Perhaps more favorable results would be seen with these two different deposition techniques if more participants utilizing these technologies would have participated.

The antireflection coatings with silica tended to have the best laser resistance. Multilayer coating designs incorporating hafnia tended to have the highest laser resistance. Surprising the fluoride and alumina coatings did not perform better because these materials transmit deeper into the UV and there has been significant development of fluorides for UV mirrors. Coatings with scandia also tended to be less laser resistant, but the limited sample number makes it difficult to draw any meaningful conclusions about the effectiveness of this material.

Simpler coatings tended to be the most laser resistant; however, the trend of laser damage resistance versus number of coating layers is not very strong. A stronger trend is the difference in the laser damage threshold between the best coated sample submitted by each participant and the laser damage threshold of their uncoated sample. Almost all of the coated samples had a lower damage threshold than the uncoated sample. For the few inverse cases, it is likely that there was an inconsistent quality between substrates and not the unlikely conclusion that the coating somehow increases the laser resistance of the surface. Certainly some of the participants have excellent polishing technology, but have not invested similar efforts into their UV antireflection coating technology. A small magnitude change between coated and uncoated damage thresholds indicates that the coatings are either well matched to the substrates or possibly that the coating laser resistance could be improved with better quality substrates.

Additionally figure 4 illustrates the impact of minor process changes on UV antireflection coating laser resistance. The use of a mixture for the high index material for participant A yields a more laser resistant coating for an IBS process. Participant I explored the impact of different process temperatures for resistive deposition of fluorides and observed minimal changes.

5.4 193 nm excimer high reflector

The damage morphology of the excimer mirrors tended to be catastrophic damage that completely ablated from the substrate and typically exhibited delaminated film edges. This morphology suggests an intrinsic and not macro-size defect laser damage initiation mechanism. Participants D and E deposited their mirrors on calcium fluoride substrates which appear to have no laser damage growth in the ablated zone. There is evidence of laser damage growth in the ablated zone for the remaining fused silica substrates (participants A, B, C, and F). A debris field was also evident surrounding the ablated zone for all of the samples with evidence of thermal and plasma effects.

The calculated laser damage threshold for an infinite number of shots was used for this competition. Since excimer mirrors are used in a wide range of industrial applications requiring long term operations exceeding 100 million shots at moderate power levels, it seems prudent to use a laser damage threshold that reflects the operational limit for these mirrors for an extended number of shots. There is a 70:1 difference in the zero damage probability for an infinite number of shots between the highest and lowest laser resistant samples as shown in figure 5.

Two of the participants shared their precoat substrate cleaning methods in an effort to understand the impact of substrate cleaning for identical coatings. Substrates were either hand cleaned with

methanol wipes or cleaned with an ultrasonic system. The samples were then coated in the same run to isolate run to run variables. It appears that for a well cleaned substrate (samples C-2, F-1, and F-2), there is little difference in the damage threshold regardless of the cleaning method. However, it also appears that a poorly cleaned substrate (sample C-1) will yield a low threshold so process technique is critical to achieve a high level of substrate cleanliness. There was no strong correlation between mirror layer count and laser resistance. Since all of the coatings met the greater than 97% reflectivity specification, this result is not surprising. There is, however, a much stronger correlation in laser damage resistance with deposition method and coating materials.

The coatings were deposited by either resistive heating or electron-beam deposition. Oxides were deposited only by e-beam while the fluorides were deposited by both resistive heating and e-beam. One of the participants also used plasma assist during their e-beam deposition. An examination of figure 5 clearly shows a strong impact of the deposition process and material type on the laser resistance of the mirror coatings. The hybrid processes containing e-beam deposition of the oxide materials and resistive heating for the fluoride materials tended to have lower laser resistance compared to non-mixed deposition processes. It is unknown if the mirror laser resistance is affected more by the hybrid deposition process or the commonality of the use of aluminum oxide in all of the lower threshold mirrors. One of the challenges of fluoride coatings is the intrinsic tensile stress which can lead to crazing of the multilayer coating. A solution to this problem is the addition of compressively stressed oxide materials to the coating design for stress balancing to reduce the probability of crazing problems, however, oxide materials tend to have higher UV cut-offs as illustrated in figure 1.

Coatings with aluminum oxide as a high index material clearly have the lowest laser resistance. This is very likely due to the very high UV cutoff (180 nm) of this material leading to absorption-induced laser damage. The UV cutoff of approximately 160 nm for silica is further from the test wavelength so less absorption would be expected from this oxide material. This is consistent with the higher laser resistance of the mirror samples containing silica. Unfortunately characterizing the absorption of these films is outside of the scope of this competition. A common design strategy for mirrors containing at least three different coating materials is to bury the absorbing oxide material toward the bottom of the stack (closest to the substrate). This lowers the electric field within the absorbing oxide layers, which presumably have a lower laser resistance, while adding compressive stress to the coatings balancing the tensile stress of the fluorides.

There are two coatings that have a pure fluoride design, samples D-1 and E-2. The lower laser resistant coating was deposited by e-beam whereas the higher laser resistant coating was deposited by resistive heating. From a materials perspective these two samples are quite similar suggesting that resistive heating of fluorides results in a more laser resistant coating.

The coatings with gadolinium fluoride, cryolite, and silica (F-1, F-2, and C-2) all had little degradation in laser resistance with increased number of shots. Sample C-1 which also had this same three material combination was an exception since it had a substantial degradation in laser resistance with increased shot rate. However, this sample also had the ineffective pre-coat substrate cleaning process. The highest laser damage threshold sample, E-2, had a moderate dependence on shot number. From a reliability perspective, samples F-1, F-2, and C-2 may be the preferred deposition process and material combination.

6. CONCLUSIONS

The results of this series of damage test competitions show that a wide range of laser damage threshold exists for coatings within the optical coating industry. Femtosecond and excimer coatings tended to have a smaller damage threshold range most likely due to the more intrinsic behavior at short pulselengths and short wavelengths. Alternatively, damage thresholds for 1064 nm mirrors and 351 nm antireflection coatings illuminated with nanosecond length pulses tend to have a significant variation in damage threshold indicating more stochastic defect driven damage mechanisms. Coating materials and deposition method typically has a significant impact on the laser resistance of optical coatings. The substrate cleaning method also can have a significant impact on laser damage resistance.

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Table 1 Participant list for the annual BDS thin film damage competition

Company	Country	2008	2009	2010	2011
Absolute Coatings	USA			✓	
Advanced Thin Films	USA	✓	✓		
Agilent Technologies	USA	✓			
Altechna Co LTD	Lithuania				✓
Arrow Thin Films	USA			✓	
Berliner Glas KGaA	Germany	✓			
Corning	USA				✓
Fraunhofer Institute for Surface Engineering and Thin Films	Germany		✓		
Gooch and Housego, Ilminster	United Kingdom		✓	✓	
Gooch and Housego, CCI	USA			✓	
Gooch and Housego, General Optics	USA			✓	
Institute of Optics and Electronics Chinese Academy of Sciences	China	✓	✓		
Jenoptik Laser, Optik, GmbH	Germany		✓		
Jiutle	China			✓	
Kugler	Germany	✓			
Laser Components	Germany	✓	✓		
Laser Zentrum Hannover, e.V.	Germany	✓	✓	✓	✓
Laserhof Frielingen GmbH	Germany	✓			
LaserOptik	Germany	✓			
Lawrence Livermore National Lab	USA			✓	
Layertec Optical Coatings	Germany		✓	✓	
Nikon	Japan	✓	✓	✓	✓
Optida	Lithuania	✓			
Okamoto Optics Work, Inc.	Japan		✓		
Optical Coatings Japan	Japan			✓	
Photonics Products Group Inc.	USA	✓			
Plymouth Gratings	USA	✓			
Precision Photonics Corporation	USA		✓		
Quality Thin Films	USA	✓	✓		
Schott	USA		✓		
Shanghai Institute of Optics & Fine Mechanics	China	✓	✓		✓
Spectra Physics	USA		✓		
SLS Optics	United Kingdom				✓
TelAztec	USA	✓			
Twin Star Optics	USA	✓			
University of Rochester, Laboratory of Laser Energetics	USA	✓			
VLOC	USA	✓			
Total	37	19	15	11	6

Table 2 Coating specifications

Year	2008	2009	2010	2011
Coating type	HR	HR	AR	HR
Wavelength	1064 nm	786 nm	355 nm	193 nm
Pulse length	5 ns	180 fs	7.5 ns	13 ns
Repetition rate	10 Hz	1 kHz	10 Hz	100 Hz
Reflectivity	>99.5%	>99.5%	<0.25%	>97%
Incident angle	0 degrees	0 degrees	0 degrees	0 degrees

Figure captions

Fig. 1 Published refractive index and UV cutoff values for the oxide coating materials used in these competitions.

Fig. 2 Impact of high index material and deposition process on laser resistance of 1064 nm normal incidence mirrors.

Fig. 3 Impact of high index material and deposition process on laser resistance of femtosecond mirrors.

Fig. 4 Impact of coating material and process on the laser resistance of 351 nm antireflection coatings.

Fig. 5 Impact of cleaning method (top), deposition process (middle), and coating material (bottom), on the zero probability of damage for an infinite number of pulses of excimer mirrors.